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PSEUDOANISATIN-LIKE SESQUITERPENE LACTONES FROM THE PERICARPS OF *ILLICIUM DUNNIANUM*

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Key Word Index—*Illicium dunnianum*; Illiciaceae; pericarp; sesquiterpene; 3-benzoyl-pseudoanisatin.

Abstract—A new sesquiterpene lactone, 3-benzoyl-pseudoanisatin, has been isolated from pericarps of *Illicium dunnianum*, together with the four known sesquiterpene lactones dunnianin, pseudomajucin, pseudoanisatin and 6-deoxypseudoanisatin. The structure of the new compound was established by spectroscopic and chemical methods.

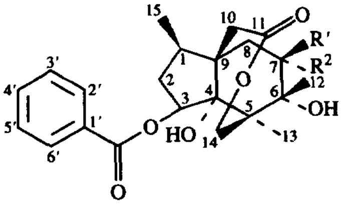
INTRODUCTION

The sequiterpene lactones 6-deoxypseudoanisatin, dunnianin and 6-deoxydunnianin have been isolated from the bark of *Illicium dunnianum* [1], which is regarded as a toxic plant and is distributed in the southern part of China. The root is used locally as an antiarthritic agent. Further research on the pericarps of *I. dunnianum* yielded a new pseudoanisatin derivative (**1**).

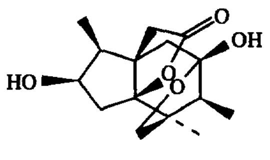
RESULTS AND DISCUSSION

The chloroform part of the methanolic extract of the pericarp of *I. dunnianum* yielded dunnianin (**2**), pseudomajucin (**3**), pseudoanisatin (**4**), 6-deoxypseudoanisatin (**5**) and a new pseudoanisatin derivative (**1**).

Compound **1** was assigned the molecular formula $C_{22}H_{26}O_7$ (EIMS, *m/z* 402 $[M]^+$; ^1H NMR, and proton count). The EI-mass spectrum showed a benzoyl ion peak at *m/z* 105 and *m/z* 77. This conclusion was



1 R', R² = O
2 R' = OH, R² = H



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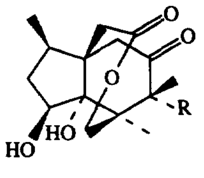

4 R = OH
5 R = H

Table 1. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) data of compound **1** in CD_3COCD_3

Position	^1H	^{13}C
1	2.60–2.70 (*m*)	39.2
2a	1.25–1.35 (*m*)	41.6
2b	2.60–2.70 (*m*)	
3	4.54 (*d*, $J = 5.1$)	80.3
4		82.0[a]
5		51.0[b]
6		80.5[a]
7		209.0
8a	2.55 (*d*, $J = 20.1$)	41.5
8b	2.74 (*d*, $J = 20.1$)	
9		50.3[b]
10a	2.11 (*d*, $J = 13.2$)	34.7
10b	3.33 (*d*, $J = 13.2$)	
11		169.5
12	1.35 (*s*)	18.4
13	1.51 (*s*)	16.1
14a	4.34 (*d*, $J = 13.6$)	66.6
14b	4.41 (*d*, $J = 13.6$)	
15	0.96 (*d*, $J = 6.9$)	14.9
$C_6H_5\underline{C}O$		166.0
1'		131.0
2', 6'	7.94 (*d*)	130.0
3', 5'	7.50 (*t*)	129.2
4'	7.63 (*t*)	133.8

[a,b] Assignments may be interchanged.

also confirmed by the ^{13}C NMR signals (δ *c*, 166.0, 133.8, 131.0, 130.0 and 129.2). The IR spectrum indicated the presence of carbonyls (ν_{max}: 1751.1 cm^{-1}, 1722.4 cm^{-1}) and hydroxyl groups (ν_{max}: 3414.3 cm^{-1}).

The ^{1}H NMR spectrum contained two tertiary methyl signals at δ_H 1.35 and δ_H 1.51, a doublet methyl signal at δ_H 0.96 and three sets of signals for isolated methylene groups (H_2-8, H_2-10, and H_2-14). The highfield ^{13}C NMR data are similar to those of pseudoanisatin (Table 1). The proton connectivities H_3-15–H-1–H_2-2–H-3 were established by ^{1}H–^{1}H two dimensional correlation spectroscopy. All of these findings indicated that the compound had a pseudoanisatin-like core. On alcoholysis it gave pseudoanisatin. This further confirmed that it was a derivative of pseudoanisatin. The ^{1}H NMR spectrum of this compound in DMSO-d_5 showed that the signals of H-3 as a doublet, i.e. the same as in pseudoanisatin. Thus the hydroxyl moiety at C-3 in pseudoanisatin has been replaced by a benzoyl group in compound **1**.

EXPERIMENTAL

General. Mps, uncorr.; IR: KBr discs; MS: MM70-70H spectrometer; NMR: 300 MHz (^{1}H) and 75 MHz (^{13}C) with TMS as int. standard.

Plant material. The fruits of *I. dunnianum* Tutch were collected at Longsheng, Guangxi Province, China, in Aug. 1992. The species was determined by Prof. Chunshu Y. (Beijing University of Traditional Chinese Medicine).

Extraction and isolation. The dried, powdered pericarp of *I. dunnianum* (4.0 kg) was extracted with MeOH at room temp. The extract was evapd to give a brown gum (1.03 kg) which was dissolved in water and partitioned against hexane, $CHCl_3$ and EtOAc, respectively. The $CHCl_3$ phase was evapd and the residue (8.8 g) subjected to silica gel CC (eluted with a $CHCl_3$–MeOH gradient) to give 23 frs. Fr. 14, eluted with petrol–EtOAc (1:4), gave two major compounds, **4** (0.8 g) and **5** (1.5 g). Compound **1** (90 mg) was obtained from fr. 8, **2** (30 mg) from frs 9–11, and **3** (20 mg) from fraction 12 by recrystallization.

3-*Benzoylpseudoanisatin* (**1**). Prisms (from EtOAC–*n*-hexane). IR ν_{max}^{KBr} cm^{-1}: 3413 (OH), 1751, 1722 (C=O), 3012, 1450, 715 (Φ); EIMS *m/z*: 402 $[M]^+$, 359 $[M-43]^+$, and 237 $[M-43-122]^+$; ^{1}H ^{13}C NMR: (Table 1).

Alcoholysis of compound **1**. Compound **1** (5 mg) was dissolved in MeOH (10 ml), followed by drops of conc. H_2SO_4 and the mixture was refluxed for 5 hr at 80°. The solution was then neutralized with NaOH to pH 7, and purified by silica gel CC to yield pseudoanisatin (1 mg).

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